

Appendix G

Inexpensive method for coating the interior of silica growth ampoules with pyrolytic boron nitride

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Abstract

An inexpensive method was developed for coating the interior of silica ampoules with hexagonal boron nitride. An aqueous solution of boric acid was used to coat the ampoule prior to drying in a vacuum at 200°C. This coating was converted to transparent boron nitride by heating in ammonia at 1000°C. Coated ampoules were used to achieve detached solidification of indium antimonide on earth.

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1. Introduction

Pyrolytic boron nitride (PBN) crucibles and boats are often used for Bridgman crystal growth of compound semiconductors (see, for example, a 1990 review [1]). This material is relatively non-contaminating, is not wet well by these melts [2-7], and does not adhere strongly to growing crystals. Unfortunately PBN crucibles are also expensive, fragile and opaque. Being non-fusible, they are usually placed inside silica ampoules that are sealed prior to growth. With their highly anisotropic thermal conductivity, they are also thought to make it difficult to control the shape of the freezing interface [8-10]. For these reasons, a method for coating the interior of a growth ampoule with a film of PBN was developed in this laboratory in 1995 [5,12]. Borazine ($B_3N_3H_6$) vapor at $\sim 10^{-4}$ Torr was passed through the interior of an ampoule at 1100°C that had been sealed at one end. After 1 h this yielded a transparent film of BN. When used in Bridgman growth of In-doped CdTe, there was no adhesion of the crystal which exhibited only 1.5×10^5 etch pits that were distributed randomly, rather than being in the cellular pattern of low-angle grain boundaries typical of growth in uncoated or carbon-coated ampoules [11,12]. Recently, we showed that detached solidification of InSb can be achieved on earth using a PBN coating to increase the contact angle of the melt on the wall [34,36].

Although borazine is a very convenient precursor for coating the interior of silica ampoules, it is rather expensive and difficult to obtain. It must be stored at low temperature in order to slow its decomposition to hydrogen and an inorganic polymer. Thus, we searched for a simple technique using more common chemicals as precursors. There is a rich literature on vapor

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deposition of boron nitride. A brief review of the more relevant papers follows.

The literature on BN deposition was reviewed in 1988 [13] and again in 1990 [14]. There was no mention of coating ampoules for crystal growth. In 1989, sandblasted silica boats were coated with BN using BCl_3 and NH_3 in Ar at 1020 to 1120°C [15]. These were used for synthesis of GaAs. Although there was no adhesion or decomposition, the resulting GaAs was contaminated with Si. A silica ampoule for physical vapor transport of CdTe was believed to have been coated with BN by covering the interior surface with BN powder and heating the exterior with an oxy-hydrogen torch. The resulting CdTe crystals were single without precipitates, but apparently doped with B.

Borazine has been used to deposit BN by several other investigators. For example, plasma-enhanced CVD was used to deposit BN from a hydrogen-borazine mixture at 550°C on unspecified substrates [16]. A hot filament at ~1400 °C was used to deposit BN on Si, silica and KBr from 100 to 400 °C [17]. Polyborazine dissolved in tetrahydrofuran was spin-coated on Si and oxidized Si wafers, and then pyrolyzed by heating at 5 °C/min to 900 or 1100 °C [18].

A mixture of cubic and hexagonal BN was deposited on Si, Ni and NaCl at 300 to 500°C using trimethyl borazine [19]. Hexagonal BN was produced at 880 to 1050 °C from a mixture of trimethyl borazine, NH_3 and H_2 [20]. Triethyl borane and trimethoxyborane were used to prepare BN for x-ray lithography masks [21]. Boron triazide ($\text{B}(\text{N}_3)_3$) was used in an Ar plasma to deposit BN at 400 °C on Si and N [22].

A common reactant mixture to produce PBN is diborane (B_2H_6) plus NH_3 [e.g., 23-25]. However, diborane is toxic, pyrophoric, and reactive [26]. Transparent films of BN were deposited on silica from 400 to 750°C using atomic layer epitaxy with BBr_3 and NH_3 [27]. A similar process was used to deposit BN on ZrO_2 particles at 500 K [28]. Boron trichloride and diborane were used under a variety of conditions to deposit BN from 500 to 1300°C [29]. Boron tribromide and trichloride are skin, eye, and respiratory irritants that can be fatal [30,31].

The previous reactants and methods for depositing PBN all suffer from one or more of the following disadvantages: the reactants are expensive or not available commercially, the reactants are toxic and difficult to dispose of, or the method requires a low pressure or plasma. Two papers suggested that a suitable BN coating can be produced by reacting non-toxic boric acid (H_3BO_3) with ammonia. In one, boric acid was evaporated in an ammonia plasma to yield BN on substrates as low as 450°C [32]. In the other, ceramic fibers were dip-coated in a boric acid solution followed by reaction with ammonia [33]. It is this latter route that we followed to develop a method to coat the interior of fused silica growth ampoules with BN.

2. Coating method

The details of the experimental methods are given in reference [34]. A 9-mm ID silica tube was sealed at one end with a conical tip and length of 15 cm, and then thoroughly cleaned. A saturated solution of boric acid in deionized water was prepared at 80–90°C. The ampoule was filled with this hot boric acid solution. The ampoule was immersed in a beaker containing cold water for a short time. No solid was observed in the ampoule. The beaker was placed in an ultrasonic bath for several seconds until a small amount of white material was observed. The solution was poured out. A thin, even layer of solid particles could be observed on the interior surface of the ampoule. This short ampoule was fused to a long uncoated fused silica tube to form a ~60-cm long ampoule.

The boric acid coating was converted to boron nitride by reacting it with ammonia in a

horizontal three-zone split furnace, as shown in Fig. 1. The short ampoule coated with boric acid was placed inside a larger diameter silica tube. Ammonia gas was fed in by a 4-mm OD \times 3-mm ID silica tube that ran to the end of the ampoule. The system was evacuated to about 0.03 Torr and heated to 200°C for 2 h in order to convert the boric acid to boron oxide. A layer of white material could be observed on the interior surface of the ampoule. The furnace temperature was increased to 600°C and held for 2 h. The white coating became transparent on the interior surface of the ampoule. It is believed that the boron oxide had melted onto the fused silica surface. The valve to the vacuum pump was closed. The pressure was increased to 50 kPa with ammonia gas and then to 60 kPa with forming gas (10% H₂ in Ar). At the same time, the temperature was increased to 1000°C and held for 5–8 h. Then the tube was alternately evacuated and back-filled with ammonia and forming gas several times. The furnace power was turned with 0.1 Torr of ammonia pressure until the furnace had decreased to room temperature. The tube was evacuated and then flushed with forming gas.

For formation of BN, reaction temperatures of 500°C, 800°C, and 1000°C were tried before 1000°C was chosen as the best temperature. After treatment with ammonia for 20 h at 500°C or 800°C, there was a layer of grey material on the interior of the ampoule. This layer could be washed off by water or alcohol. Fourier Transform Infrared (FTIR) spectrometry showed no BN peak. After exposure to air for one day, the layer turned white. This layer was likely boron oxide left on the surface that had absorbed moisture in the air to form boric acid. After 20 h of exposure to NH₃ at 1000°C, the ampoule was transparent, sometimes with a little whitish material on parts of the ampoule inner surface. Rinsing with alcohol removed this white material, which is thought to have been loose BN particles.

3. Characterization and application of coating

After coating, Fourier Transform Infrared Spectrometry (FTIR) was used to analyze the film formed as above. The surface of the samples was examined using the diffuse reflection method rather than transmission or absorption. Figure 2 shows the FTIR spectrum of a small piece from a coated ampoule that had been deliberately broken after coating for 20 h. The \sim 1380 cm⁻¹ wavenumber corresponds to the B-N stretching vibration [5,12,21,29,35]. No peak was observed at 800 cm⁻¹, which corresponds to the B-N-B stretching mode. We conclude that the structure of the boron nitride was hexagonal.

The contact angle of a sessile water drop was greatly increased by the BN coating, as shown in Fig. 3.

Our BN coating proved essential in obtaining detached solidification of InSb by vertical Bridgman growth on earth [34,36].

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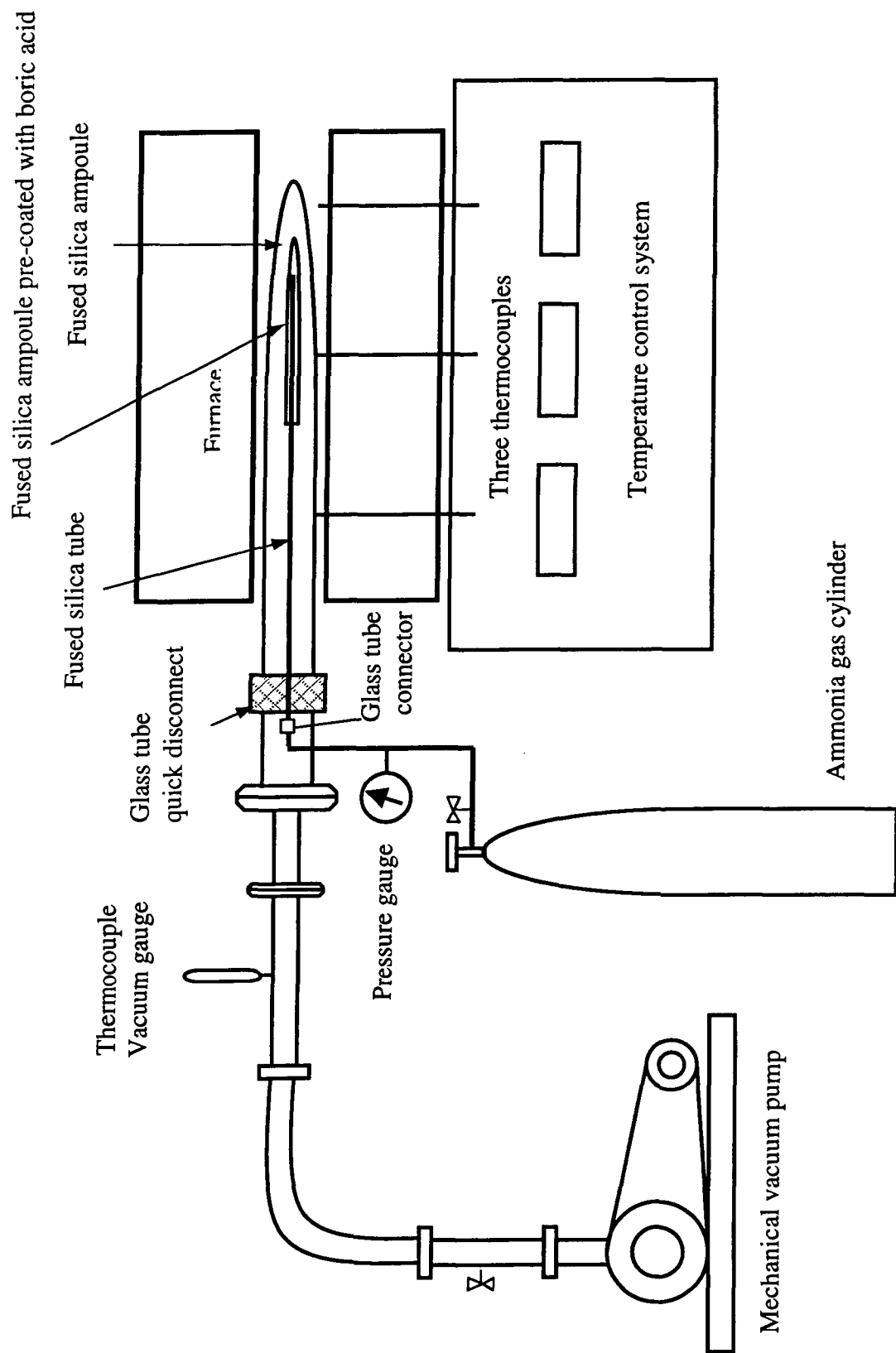


Fig. 1. Apparatus for conversion of boric acid to boron nitride

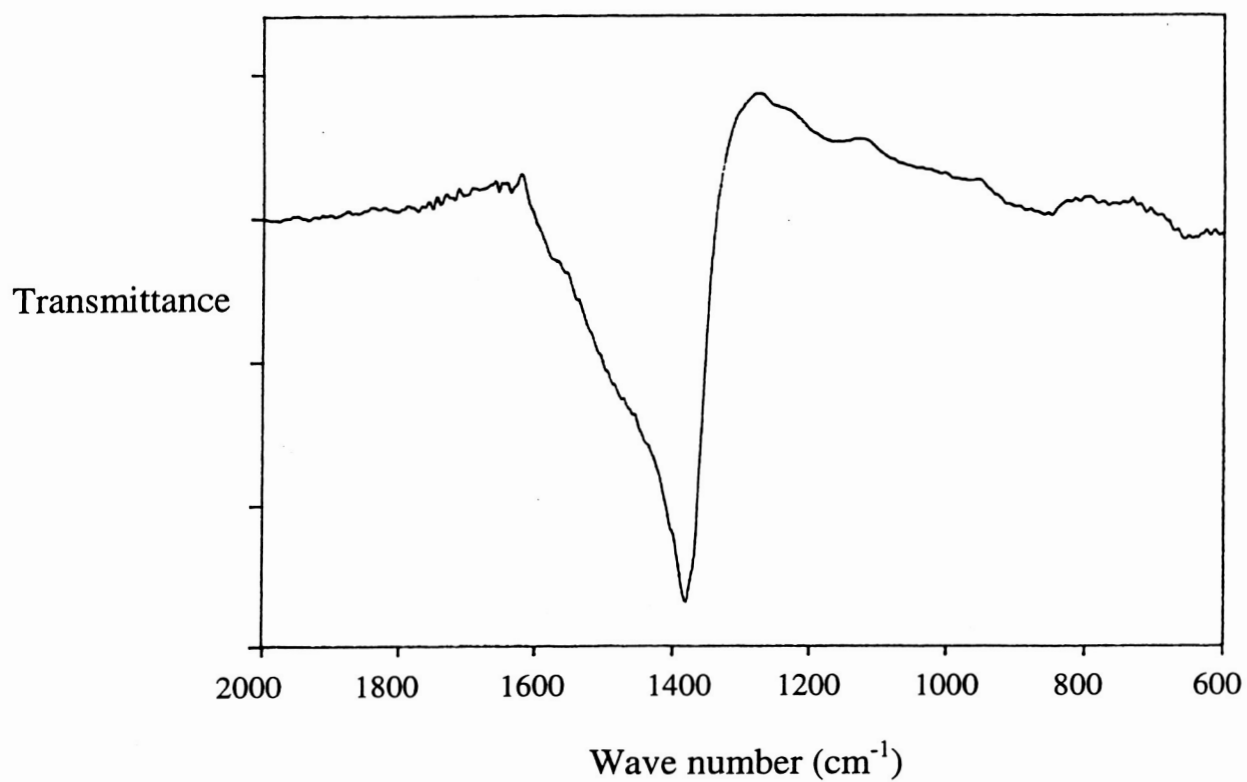


Figure 2. Infrared spectra of BN coating on fused silica plate

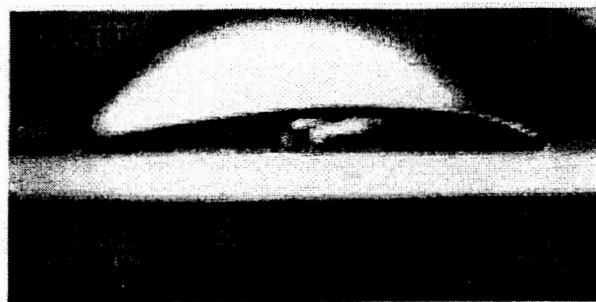


Fig. 3. Sessile water drop on fused silica plate.
Left: clean and uncoated
Right: BN coated